# Ground-based observations of Arctic $O_3$ loss during spring and summer 1997

G.C. Toon, J.-F. Blavier, B. Sen, R.J.Salawitch, G.B.Osterman,
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

J. Notholt, M.Rex,
Alfred Wegener Institute, Potsdam, Germany

C.T.McElroy,
Atmospheric Environment Service, Environment Canada, Downswiew, Ontario

P.Newman,
Goddard Space Flight Center, Greenbelt, Maryland

J.M.Russell III,
Hampton University, Hampton, Virginia

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**Abstract:** Ground-based solar absorption spectra were measured from Fairbanks, Alaska (65°N, 148°W) and from Ny Alesund, Spitsbergen, (79°N, 12°E) from March to September 1997 by Fourier Transform Infra-Red (FTIR) spectrometers. These spectra have been analyzed to determine the vertical column abundances above the sites of various atmospheric gases including HF, HCl, $ClNO_3$, NO, $NO_2$, $HNO_3$, and $O_3$. Maps of potential vorticity and HF column abundances indicate that the observations made from Fairbanks were almost entirely made outside the vortex, whereas those measured from Ny Alesund were continuously inside the vortex until early May, a full month later than normal. Depleted amounts of ozone were observed throughout the spring from Ny Alesund. Although the ozone recovered in mid-May following the break-up of the winter vortex, further $O_3$ loss (25%) occurred during the summer, above both Fairbanks and Ny Alesund. This $O_3$ loss was accompanied by no change in the HF column abundances, or in the partitioning of chlorine species. However, a summertime maximum in the $NO_X/NO_Y$ column ratio was observed, and so we conclude that the summertime $O_3$ loss was likely driven by $NO_X$ chemistry. It is further shown from balloon and satellite data that the $O_3$/HF ratio decreases with increasing latitude throughout the stratosphere. Thus, the observed 25% summer loss of column $O_3$ is likely an underestimate of the true chemical loss because any meridional transport would have increased the $O_3$/HF column ratio, mitigating the chemical loss.

## Introduction.

It has long been known that the vertical column of ozone declines substantially during the high latitude summer [e.g. *Fioletov et al.*, 1997]. Unlike the wintertime $O_3$ loss, which is mainly due to chlorine chemistry [*McKenna et al.*, 1990; *Salawitch et al.*,1990], the summertime $O_3$ loss is believed to be a natural phenomenon caused by photochemical processes enhanced under the long hours of daylight [*Johnson*, 1975; *Farman*, 1985]. However, in the absence of simultaneous measurements of $O_3$, $NO_X$, and tracers of transport, it has not been possible to accurately quantify

the relative contributions of transport and the various chemical loss mechanisms to this summer ozone loss.

During the spring and summer of 1997, a co-ordinated campaign of balloon, aircraft, and ground-based measurements of the atmospheric composition was conducted from Fairbanks, Alaska (65$^{o}$N, 147$^{o}$W), in order to gain a more quantitative understanding of the reasons for ozone loss observed during the high latitude summer. As part of the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) campaign, the JPL MkIV interferometer performed two balloon flights (8 May and 8 July 1997) from Fairbanks and also made 47 days of ground-based column observations over the March-September period.

In this paper we examine the MkIV ground-based columns measured from Fairbanks, Alaska, in 1997 and from Lynn Lake, Manitoba (57$^{o}$N, 101$^{o}$W), in 1996, together with measurements made by a similar instrument from the Network for Detection of Stratospheric Change (NDSC) station in Ny Alesund, Spitsbergen (79$^{o}$N, 12$^{o}$E). We show how these combined datasets, taken at different latitudes, provide a more complete picture of the seasonal evolution of the stratospheric trace gases, and the magnitude of the spring- and summer-time ozone losses, than would be possible from a single site. Together with balloon and satellite profiles of the key gases, these ground-based observations are used to investigate the causes of high latitude summertime $O_3$.

## Instruments.

The ground-based column measurements were performed by Fourier Transform Infra-Red spectrometers operated in solar absorption mode. The Fairbanks and Lynn Lake observations were made by the MkIV interferometer, which was built at the Jet Propulsion Laboratory (JPL) in 1984 specifically for atmospheric remote sounding [*Toon*, 1991]. The MkIV instrument uses parallel $LN_2$-cooled HgCdTe and InSb detectors to cover the entire 700 to 5700 cm$^{-1}$ spectral region simultaneously. An optical path difference (OPD) of 117 cm was employed, corresponding to a spectra resolution of about 0.006 cm$^{-1}$. The Ny Alesund observations, described in more detail by *Notholt et al.* [1997], used a commercial IFS120HR spectrometer manufactured by Bruker. The IFS120 used a slightly higher OPD (157-200 cm) and covered the same spectral range as the MkIV, but not simultaneously: interference filters were generally employed to narrow the spectral range, hence increasing the signal-to-noise ratio in the remaining spectrum. The broad spectral coverage and high spectral resolution of both instruments allowed over 20 different gases to be measured from the ground.

## Data Analysis.

The ground-based spectra from both the MkIV and the IFS120 instruments were analyzed using an algorithm developed at JPL for least squares fitting of solar absorption spectra. This algorithm fits a calculated spectrum to each measured spectrum in a least squares fashion by adjusting the assumed vmr profiles. The atmosphere is represented as a 100 level model and for each level line-by-line calculations are performed to determine the absorption spectrum. The contribution of each level to the total slant path is determined by ray tracing.

At the high solar zenith angles employed for many of these observations, the retrieved vertical column abundances are fairly sensitive to the assumed shapes of the vertical volume mixing ratio (vmr) profiles. For most gases the shape of the vertical profiles cannot easily be

determined from ground-based spectra. Hence we adopted the set of vmr profiles retrieved from the May 1997 MkIV Fairbanks balloon flight. Of course, inside the winter vortex, there is much more subsidence than during the summer, so these balloon profiles could not be used directly. However, satellite observations [*Abrams et al.*, 1996a and 1996b] have shown that the isopleths inside the winter vortex are related to non-vortex isopleths by a simple vertical scaling such that the amount of descent is directly proportional to the altitude above the tropopause. This allowed us to determine the degree of subsidence (DOS) appropriate to each observation from the HF and $N_2O$ lines, apply it to all the other trace gas profiles according to the equation

$$VMR(Z) = VMR_{ref}( Z_T + (Z-Z_T)/(1+DOS) )$$

where $Z_T$ is the tropopause altitude, as described by *Notholt et al.* [1997]. Note that this process preserves the tracer correlations present in the original balloon profiles, since only the altitudes are adjusted, not the vmrs themselves. The resulting scaled vmr profile set was used for our initial guess for the analysis of each day's observation. Temperature profiles taken from sondes, were used in the line-by-line calculations of the spectral absorption coefficients at each atmospheric model level. Climatological temperature profiles were used for altitude above the upper limit of the sondes (typically 30 km).

In addition to using the same spectral analysis algorithm (including molecular spectroscopic parameters) for the analysis of the Fairbanks, Lynn Lake, and Ny Alesund spectra, we also used the same initial vmr profile set (before vertical scaling), and fitted the exact same spectral intervals. In this manner we hoped to minimize the risk of introducing systematic biases between the data acquired from the three sites.

## Data Validation.

Figure 1a illustrates a comparison of $O_3$ column abundances measured above Fairbanks by the JPL MkIV interferometer, the Earth-Probe TOMS instrument, and a Brewer spectrophotometer, the latter located just 20 m from the MkIV instrument. These measurements show that the $O_3$ column fell from around $11.5x10^{18}$ molec.cm$^{-2}$ (425 Dobson Units) in late March (day 90), to about $7.5x10^{18}$ molec.cm$^{-2}$ (275 DU) in September. This decrease was not monotonic: mimima in $O_3$ column can be observed around days 177 and 217 which are believed to be related to transport from higher latitude. Given the very different assumptions about the vertical distributions of $O_3$ and temperature adopted in the analysis of the observations, the agreement (always better than 5%, and usually 2-3%) achieved between these three different measurement techniques is excellent and demonstrates their good accuracy and precision. A more detailed comparison of $O_3$ column measurements above Fairbanks during POLARIS is presented by Lloyd et al. [1999].

Validation of the column abundances of the other gases (e.g. HF, HCl, $HNO_3$, $NO_2$, $ClNO_3$) is much more difficult. Although most of these gases are measured by the HALOE instrument on board the UARS satellite, it is notoriously difficult to derive an accurate total vertical column abundance from a satellite-derived profile because of the poor sensitivity of the latter to altitudes below the peak concentration. Furthermore, HALOE does not obtain any data at high latitudes ($> 60^{O}$) in mid-summer. A companion paper [*Toon et al.*, this issue] shows good agreement between MkIV balloon profiles of several of these gases with in-situ measurements

from the ER-2 aircraft. However, the gases compared do not include the important tracer HF, since it is not measured by any instruments on board the ER-2.

## The Problem.

The main problem addressed in this paper is illustrated by Figure 1, which shows average daily vertical column abundances of (a) $O_3$ and (b) HF measured from Fairbanks in 1997. Ignoring the vortex influenced points around day 105, it is apparent that the $O_3$ column fell by 35% between late March and late September, whereas the HF column did not show any significant decline over the same period. As shown later, at high latitudes HF is a long-lived tracer with a vertical concentration profile similar in shape to that of $O_3$, so that large scale vertical transport will tend to change the $O_3$ and HF column abundances proportionately. Furthermore, $O_3$/HF ratio decreases with increasing latitude throughout the stratosphere, making it difficult for meridional transport to decrease $O_3$ but not HF. This all suggests that the summertime loss of $O_3$ must be mainly due to chemistry, for it is difficult to conceive of a large-scale transport process which could remove $O_3$, but not HF, from the high latitudes.

To place this conclusion on a firmer foundation, we sought to further investigate our assumptions: (i) that HF is a good tracer of stratospheric transport, and (ii) that the HF and $O_3$ profiles are sufficiently correlated that transport effects will change their vertical column abundances proportionally. We also sought to confirm that the behavior of $O_3$ and HF observed from Fairbanks in 1997 was consistent with that from other high latitude sites, and with observations from earlier years. Furthermore, we wanted to test whether the measured column abundances of other relevant gases (e.g. HCl, $ClNO_3$, $NO_2$, $HNO_3$, $NO_X$) were consistent with our hypothesis of the summertime $O_3$ loss being mainly due to chemistry.

## Investigating the HF-$O_3$ relationship with balloon and satellite data.

To test the assumption that HF is a good tracer, we present in the upper panel of Figure 2 MkIV balloon vmr profiles of HF and $N_2O$. The latter is a well-understood and often-used tracer of stratospheric transport [e.g. *Keim et al.*, 1997]. The spread in the HF-$N_2O$ correlation plot is mainly a consequence of the large rate of increase in HF (about 5% per year), since the $N_2O$ increase (0.35% per year) is negligible by comparison. This can be shown by defining a detrended HF vmr (HF*) such that

$$HF^* = HF \times [\, 1 - 0.055 \times (T-1996) \,]$$

where T is the time of the measurement expressed in years. The linearity of the $HF^*$-$N_2O$ correlation (Figure 2b) together with its tight correlation confirms that $HF^*$ is indeed a long-lived tracer of stratospheric motion [*Plumb and Ko*, 1992]. The time correction described above will also be applied to the HF vertical column abundances, allowing us to quantitatively compare HF column abundances measured in different years. Henceforth, all discussion of HF will refer to the detrended values defined by the equation above.

The absence of significant tropospheric HF [*Sen et al.*, 1995], which is due to its high solubility in water, makes its column much more sensitive to transport-induced changes in the stratosphere than a tropospheric source gas like $N_2O$. For example, when the vortex came over Fairbanks around day 105 the HF column abundance increased by about 55% due to the enhanced subsidence of the vortex airmasses. The $N_2O$ column abundance, on the other hand, decreased by just 3%. Thus, small variations in the tropospheric vmr of $N_2O$ or the surface

pressure could easily mask or confuse the stratospheric changes of interest, making ground-based observations of column $N_2O$ a poor diagnostic of stratospheric transport. Note that the balloon profiles $N_2O$ do not suffer from this problem because the stratospheric measurements are without tropospheric interference.

Figure 3 shows vmr profiles of HF, and $O_3$ measured by MkIV above Fairbanks during balloon flights in May and July 1997. The HF profiles have been scaled by a factor of 5000 in this figure to bring them to a similar value as the $O_3$ profiles. Figure 4 shows the same profiles, but plotted as concentrations (molec.cm$^{-3}$). This is because it is the integral of the concentration with respect to altitude (i.e. the area under the curves) that represents the vertical column abundance. It is important to recognize that although the HF vmr profile peaks above 40 km and the $O_3$ vmr profile peaks around 32 km, the vast majority of the HF and $O_3$ molecules nevertheless reside in the 12-28 km altitude range. Therefore, the ground-based HF and $O_3$ column abundances are most sensitive to transport and chemistry occurring in the 15-25 km altitude range, not the altitude of their peak vmrs. The strong similarity in the shapes of the vmr and concentration profiles of these gases over the altitude range relevant to ground-based observations, suggests that vertical transport will have similar effect on both species. Therefore, ratioing the column abundances of any of these gases to that of HF should, to first order, remove the effects of vertical transport.

Figure 5 shows these same MkIV balloon vmr profiles of $O_3$ and HF in a different way. The upper panel shows the $O_3$-HF tracer correlation for the various mid- and high-latitude balloon flights. The symbols are color coded according to the latitude at which the measurements were made (green 30$^{o}$ to 40$^{o}$N; orange 50$^{o}$N to 60$^{o}$N; red 60$^{o}$N to 70$^{o}$N). At low vmrs of HF and $O_3$ there exists a linear regime with a reasonably tight correlation, indicating that at these altitudes (below 20 km) the lifetimes of both $O_3$ and HF must exceed the timescale for transport. At higher altitudes the mid-latitude $O_3$ increases much faster than HF. However, the high latitude data shows a much more linear relationship between $O_3$ and HF, although a modest enhancement of $O_3$ is apparent in the May 1997 Fairbanks flight at around 0.45 ppbv of HF (22 km altitude). Note that a straight line fitted through the July Fairbanks data would have a gradient of about 5000. Remember that all these balloon data were observed well away from the polar vortex, and therefore do not contradict HALOE observations made under polar vortex conditions, that show $O_3$ vmrs as low as 1 ppm at 0.8 ppb of HF [*Muller et al.*, 1997].

The lower panel of Figure 5 shows the $O_3$/HF ratio plotted as a function of potential temperature. Data acquired at and below the tropopause (HF < 4 x10$^{-11}$) are not plotted here since HF is so close to zero that the ratio becomes very noisy. Above 500K (~21 km altitude) the $O_3$/HF ratio is clearly much larger (up to a factor of 3) at mid-latitudes than at high latitudes. At lower altitudes the latitude gradient is less apparent, however, there are virtually no mid-latitude airmasses with $O_3$/HF ratios as low as 5000.

Figure 6 shows HALOE observations of $O_3$ and HF acquired during late April and the first half of May 1997. The upper panels show the $O_3$-HF correlation and the lower panels show the $O_3$/HF ratio as a function of potential temperature (PT). PT is chosen as a vertical ordinate because air parcels undergoing adiabatic motion, such as might happen during meridional transport, follow surfaces of constant PT. Data points from below 350 K have been omitted due to their proximity the tropopause where the very small HF values can cause large uncertainties in the $O_3$/HF ratio.

These data confirm the conclusion drawn from the MkIV balloon profiles that the $O_3$/HF ratio decreased with increasing latitude throughout the stratosphere. Paradoxically, the HALOE Southern hemisphere high and mid-latitude observations appear much more similar to the MkIV profiles from Fairbanks than do the HALOE Northern hemisphere observations. Our explanation for this is that the MkIV and the southern HALOE observations were made in airmasses not influenced by the polar winter vortex, whereas the northern mid and high-latitude observations included airmasses which had undergone substantial descent and chemical $O_3$ loss. Remember that in early May 1997, the Arctic polar vortex still lingered over northern Europe and Russia, giving rise to a large amount of scatter in the northern hemisphere $O_3$-HF relationship. For example, the very low $O_3$ vmrs of 1 ppm around 0.5 ppb of HF in the $56^{O}$ to $68^{O}$N latitude range were vortex airmasses and gave rise to $O_3$/HF ratios as low as 2000 in the 450 to 550 K potential temperature range (17-23 km altitude). This interpretation is supported by the non-existence of such airmasses in the southern hemisphere, where the distribution of atmospheric constituents was much more zonal and chemical loss of $O_3$ had not yet occurred.

The lines drawn on each of the panels in Figure 6 describe the average relationship in each of the specified latitude bins. These lines have been added to help the reader more easily determine the true latitude dependencies in situations where the points are widely scattered (e.g. northern high latitudes). These lines reveal that at all stratospheric altitudes the $O_3$/HF ratio decreases poleward, which means that transport of mid-latitude air to high latitudes can only increase the $O_3$/HF ratio. Therefore, to account for the low $O_3$/HF ratios in the Arctic summer, it appears that chemical destruction of $O_3$ is the most likely possibility. However, before reaching this conclusion, we should investigate (i) $O_3$ and HF column abundances from other sites, (ii) $O_3$ and HF column abundances from earlier years, and (iii) column abundances of other gases which might be relevant to the problem being addressed.

## Column Results.

Figure 7 shows the time evolution of the daily average column abundances of HF, $O_3$, HCl, $ClNO_3$, $NO_2$, $HNO_3$, $NO_X$ (the sum of NO+$NO_2$ columns) above Fairbanks (filled orange diamonds) and Ny Alesund (filled blue triangles) during 1997. For comparison with earlier years, the Ny Alesund column data from 1992-1996 are included (empty green triangles). Also plotted are MkIV column abundances measured from Lynn Lake, Manitoba ($57^{O}$N, $101^{O}$W) in July and August 1996 (empty red diamonds) in order to illustrate the latitude gradients of several of the gases under consideration.

Figure 7a illustrates the PV calculated by the GSFC model for the 460K level (~20km altitude) above Fairbanks and Ny Alesund in 1997. Above Fairbanks it was fairly constant during the spring and summer except for a few days in late March (around day 90) and again in mid April (around day 105) when the vortex edge moved slightly to the south of Fairbanks. In contrast, the larger PV values above Ny Alesund indicate that this site was continuously under the vortex until early May (Day 130). Maps of PV (not shown) indicate that the vortex actually remained intact for an few additional days before breaking apart around day 140. For the remainder of the spring and summer the PV above Fairbanks and Ny Alesund remained very flat.

Figure 7b shows that above Fairbanks in 1997, the stratospheric tracer HF displayed a surprisingly constant column abundance of $1.6\pm0.1 \times 10^{15}$ molec.cm$^{-2}$, except for the few days in late March and mid-April when the vortex edge moved over Fairbanks. Above Ny Alesund,

the 1997 springtime HF columns were much larger (typically $2.5 \times 10^{15}$ molec.cm$^{-2}$), until day 130 after which they were fairly constant at around $1.75 \pm 0.1 \times 10^{15}$ molec.cm$^{-2}$. The strong correlation between HF and PV at both sites supports the interpretation of the springtime variations of the HF column abundances as being due to movement of the polar vortex. Note that the HF column abundances above Fairbanks around day 105 when the vortex pushed south are very similar to those observed over Ny Alesund for most of the spring. Figure 7b also illustrates how in the years 1992-1996 the vortex above Ny Alesund was always gone by day 100, whereas in 1997 it persisted a full month longer.

Two important features of the HF column abundances are apparent from Figure 7b: (i) ignoring the vortex-influenced points (PV > $25 \times 10^{-5}$), there was little seasonal variation in the HF columns at either Fairbanks or Ny Alesund in 1997, (ii) there was little seasonal variation in column HF above Ny Alesund in earlier years, and (iii) a significant poleward latitude gradient of HF exists. This latter point is emphasized by the MkIV data points taken from Lynn Lake in 1996 (open red diamonds), and could have been further emphasized by noting that the average summertime HF column measured by MkIV at JPL (34$^{o}$N) is $0.85 \times 10^{15}$, which would be too small to even appear in Figure 7b. This latitude gradient is confirmed by earlier airborne column measurements [*Toon et al.*, 1994].

In contrast to HF, the $O_3$ columns, illustrated in Figure 7c, exhibit only a slight latitude gradient and exhibit a significant decrease with time. The Fairbanks data (filled orange diamonds) show a 35% decline from about $11.5 \times 10^{18}$ molec.cm$^{-2}$ in late March to about $7.5 \times 10^{18}$ molec.cm$^{-2}$ in late September. The Ny Alesund $O_3$ data measured before day 130 were inside the vortex and show considerably smaller $O_3$ columns than were measured from Fairbanks. However, as the vortex moved away from Ny Alesund in early May 1997 (days 120 to 130) the $O_3$ columns came into agreement (and even overshot) the Fairbanks values and with those observed at Ny Alesund in earlier years.

Interestingly, many of the day-to-day variations in $O_3$ mirror those in HF, suggesting that they are transport driven. For example, there are minima in $O_3$ and HF on day 257 followed by peaks on day 261. We therefore have plotted in Figure 7d the ratio of the $O_3$ to the HF column abundances. For reasons explained previously, this ratio should be less sensitive to the effects of transport than the individual gas columns themselves, and should therefore allow a more precise determination of the seasonal trend and latitude gradient in $O_3$. Ignoring for now the vortex-affected observations, Figure 7d shows an approximately 10%/month decrease in the $O_3$/HF column ratio during the summer at both Fairbanks and Ny Alesund. The Lynn Lake data are too short a time series to derive a meaningful trend. Figure 7d also shows the excellent consistency of the summertime behavior of the Ny Alesund $O_3$/HF column ratios between 1997 (blue triangles) and the earlier years (green triangles), proving that the summertime $O_3$ loss in 1997 was typical. Figure 7d also illustrates the strong summertime latitude gradient in the $O_3$/HF ratio, which we further emphasize by noting that at JPL (34$^{o}$N) this ratio varies from 7500 in winter to 9000 in summer, which would have been off the top of the panel had we tried to plot it. The similarity of the Fairbanks and JPL $O_3$/HF column ratios in springtime is testimony to the strength of meridional transport in the spring. However, the reduced summertime meridional transport allows a large latitude gradient to develop in the $O_3$/HF column ratio.

Note how the $O_3$/HF column ratios in early May and early July 1997 (6600 and 5500 respectively) are in excellent agreement with the balloon profile ratios presented in Figure 4b.

It is also apparent from the $O_3$/HF ratio that the vortex airmasses which came over Fairbanks in mid-April (around day 105) were substantially depleted in $O_3$, but not quite to the same extent as the airmasses over Ny Alesund. However, looking at the Fairbanks $O_3$ columns themselves, no effect of the vortex is apparent; the chemical losses having been compensated by subsidence.

Figure 7d allows us to estimate the loss of column $O_3$ during the 1996/1997 winter above Ny Alesund due to chemistry. In late September 1996 the $O_3$/HF column ratio was about 4100. If we assume that the airmass that subsequently became the polar vortex had a similar $O_3$/HF ratio, then the drop in the $O_3$/HF column ratio to 3100 by March 1997, a 25% decrease, must be due to chemistry. Actually this figure is probably a lower limit due to leakage of mid-latitude air carrying large $O_3$/HF ratios into the polar vortex. This 25% decrease is in good agreement with 3-D model simulations performed by *Lefevre et al.* [1997] who estimated a chemical $O_3$ loss of 60 to 120 DU (out of 350 DU). It also consistent with $O_3$ loss rates inferred from differences in sonde profiles lying on a common, computer-calculated, trajectory [*Rex*, private communication].

The springtime $O_3$/HF column ratio over Alaska (7000) exceeded that observed over Ny Alesund (3100) by more than a factor of two in 1997. This large difference is a result of meridional transport of $O_3$-rich air from mid-latitudes in the spring [Dobson, 1946; Bojkov, 1988]. Although these airmasses can easily reach Alaska, the vortex edge presents a barrier to further poleward transport, preventing significant enhancement of the $O_3$/HF ratio above Ny Alesund until the vortex is pushed away or breaks up.

After the vortex moved away from Ny Alesund around day 130, so that both sites were outside the vortex, the $O_3$/HF ratios (around day 135) became very similar at both Fairbanks and Ny Alesund at around 5800. However, in the following week this ratio dropped to 4900 at Ny Alesund. Interestingly, this is the week when the 1997 Arctic vortex finally broke apart, suggesting that this abrupt drop in the $O_3$/HF ratio may have been due to dilution of mid-latitude air by $O_3$-poor and HF-rich vortex remnants. The unfortunate absence of MkIV during the period from day 140 to 165 (due to instrumental problems) makes it difficult to ascertain whether the $O_3$/HF ratios at Fairbanks and Ny Alesund diverged from a common starting point due to the decline being faster above Ny Alesund than Fairbanks, or whether they exhibit parallel declines. In either case, by summer a significant latitude gradient of $O_3$/HF had formed.

Figure 7e shows that whereas the Fairbanks HCl column abundances show only a small seasonal variation, those measured from Ny Alesund show a rapid increase in late March and April. In summer, a highly significant latitude gradient of HCl exists with typical column abundances of $6.0 \times 10^{15}$ above Ny Alesund, $5.4 \times 10^{15}$ above Fairbanks, and $4.5 \times 10^{15}$ above Lynn Lake. For the purpose of comparison, the typical summertime HCl column abundance above JPL ($34^{\circ}$N) is $2.8 \times 10^{15}$.

The plot of the HCl/HF ratio, Figure 7f, shows the depth of the winter depletion of HCl above Ny Alesund. In late March 1997 the HCl above Ny Alesund was less than half what it should have been in the absence of heterogeneous chemical destruction. Whereas in earlier years the rapid recovery of HCl occurred during break-up of the vortex, in 1997 the vortex persisted above Ny Alesund until day 130 allowing the springtime chemical recovery of vortex HCl to be observed almost to completion. It is interesting to note that even above Fairbanks, outside the vortex, a springtime recovery of HCl is apparent in the HCl/HF ratio, which increases from 2.9 in late March to a more normal value of 3.3 by early May. A similar trend is apparent in the out-of-vortex pre-1997 Ny Alesund data. Note the much lower values (2.4) of the HCl/HF ratio on

the days that the vortex was over Fairbanks, and their good quantitative agreement with the Ny Alesund values (2.2).

Figure 7g shows $ClNO_3$ column abundances. Data from Ny Alesund are not available for 1997 due to an instrumental problem, although data from earlier years are plotted. The largest Fairbanks $ClNO_3$ columns of around $4x10^{15}$ molec.cm$^{-2}$, were measured around day 105 when the vortex came over Fairbanks. The remaining out-of-vortex Fairbanks data show a springtime decline from about $3.0x10^{15}$ to $1.5x10^{15}$ molec.cm$^{-2}$.

Figure 7h of the $ClNO_3$/HF ratio shows an out-of-vortex springtime decline (from 1.6 to 1.0), similar in magnitude but opposite in sign to the increase in the HCl/HF ratio (from 2.9 to 3.3), suggesting that the springtime recovery of HCl occurred at the expense of $ClNO_3$. Thus, even outside the vortex, heterogeneously processed air was present in late March in which HCl had been converted to $ClNO_3$. Whether this was simply vortex air mixed with mid-latitude air, or whether PSC activity had actually occurred outside the vortex (perhaps due to mountain lee waves) cannot be determined from these data.

Figure 7i shows the $NO_2$ column abundances. Whereas the Fairbanks data exhibit a modest springtime increase with a summer maximum, the Ny Alesund data show a much more dramatic springtime increase. In late March the Ny Alesund $NO_2$ columns were less than half those measured above Fairbanks, presumably due to denoxification caused by earlier heterogeneous processing inside the vortex. However, by late April (day 120) the Ny Alesund $NO_2$ columns had tripled and were 40-50% larger than those measured above Fairbanks. Note that when the vortex came over Fairbanks (around day 105), the $NO_2$ column just happened to be virtually the same inside and outside the vortex. There was therefore no obvious perturbation to the Fairbanks $NO_2$ column. After the vortex moved away from Ny Alesund (day 125) the $NO_2$ column actually fell from $6.0x10^{15}$ to $5.4x10^{15}$, since by this time the subsided vortex air was richer in $NO_2$ than the surrounding airmasses. Note that the summertime $NO_2$ column at JPL ($34^oN$) is only $3.2x10^{15}$ molec.cm$^{-2}$, so that there is a 50-60% enhancement of summertime $NO_2$ at high latitudes.

The $NO_2$/HF ratio (Figure 7j) reveals the true magnitude of the springtime $NO_2$ inside the vortex, increasing from less than 1.0 in late March to 3.0 in mid-May. Since this increase is much larger than the decrease in the $ClNO_3$/HF ratio, the main source of the $NO_2$ must be $HNO_3$, with $ClNO_3$ only a minor source.

Figure 7k illustrates the $HNO_3$ column abundances. Like the other stratospheric gases, a summertime latitude gradient is evident, which would be even more apparent if the JPL ($34^oN$) column abundances, which average $9x10^{15}$ molec.cm$^{-2}$, had been included. To correctly interpret the $HNO_3$/HF column ratio (Figure 7l) it is necessary to know that the $HNO_3$/HF ratio has only a small latitude gradient [Toon et al., 1994] which is in the opposite sense to that of $O_3$ (i.e. the $HNO_3$/HF ratio normally increases poleward). Therefore the much larger $HNO_3$/HF springtime column ratios observed over Fairbanks compared with those over Ny Alesund cannot be the result of meridional transport, which would tend to decrease the $HNO_3$-HF ratio. We therefore conclude that the relatively large $HNO_3$/HF ratios above Fairbanks were the result of heterogeneous conversion of $N_2O_5$ and hence $NO_x$ into $HNO_3$. The low $HNO_3$/HF ratios observed over Ny Alesund in the spring of 1997 are the result of denitrification. Temperatures below the 194K threshold for formation of type 1 Polar Stratospheric Clouds (PSC) were present in the 1997 polar vortex until day 82 [*Coy et al.*, 1997]. It is interesting to note that the recovery of $HNO_3$

above Ny Alesund in the 1997 spring is delayed with respect to the recovery of $NO_2$ (Figure 7j). This behavior presumably results from photolysis of $HNO_3$ being the major source of the springtime increase in $NO_2$.

The column abundance of $NO_X$ in Figure 7m, was obtained simply by adding the column abundances of NO and $NO_2$. The much larger error bars in the Fairbanks and Lynn Lake $NO_X$ after day 180 arise from the difficulty of measuring NO in the presence of large slant column abundances of water vapor. In the springtime it was very easy to measure NO from Fairbanks despite the large zenith angles because it was very cold and hence dry. However, with the arrival of warmer, humid, weather in July it became difficult to measure NO. And even though it had cooled slightly by September, it was still too humid, given the large solar zenith angles, to accurately measure NO. Observations for which the uncertainty in the NO column exceeded $3x10^{15}$ molec.cm$^{-1}$ were therefore omitted from panels (m) and (n), resulting in a paucity of points after day 170 in comparison with previous panels.

Figure 7n shows the ratio of the $NO_X$ to $NO_Y$ column abundances, the latter obtained by summing the individual column abundances of $NO+NO_2+HNO_3+ClNO_3$. Note that since these were all daytime measurements, the unmeasured amount of $N_2O_5$ should have been only a small fraction of $NO_Y$, especially in the summer. Since the $NO_X$ and $NO_Y$ concentrations do not quite peak at the same altitude, these values cannot be directly compared with profile observations. Nevertheless, it is worth pointing out that MkIV Balloon observation from Fairbanks show a $NO_X/NO_Y$ ratio at 25 km altitude (the mean altitude of the $NO_X$ concentration profile) of 0.30 in May and 0.40 in July [*Osterman et al.,* 1999], values which are highly consistent with the column observations. The peak in the $NO_X/NO_Y$ column ratio in the summer is likely a consequence of photolysis converting the $NO_Y$ reservoirs (e.g. $HNO_3$, $N_2O_5$, $ClNO_3$) into $NO_X$.

## Discussion.

To place these high latitude results into a more global context, we note that whereas column abundances of HF typically increase by nearly a factor of eight between the equator and the poles, the $O_3$ column abundance increases only by a factor of two [*Toon et al.,* 1994]. This is a consequence of the HF formed in the tropics having no stratospheric sink and so its vertical column abundance increases as it is carried poleward and downward. Ozone, on the other hand, has several stratospheric loss processes which offset the column enhancement caused by descent. The resulting $O_3$/HF column ratio is therefore a strong function of latitude, decreasing from nearly 20,000 in the tropics to 5000 at high latitudes, and even lower under springtime vortex conditions (e.g. 3000 in Ny Alesund in late March 1997). Remember that the springtime $O_3$/HF column ratios above JPL (7500) are only slightly larger than those above Alaska. However, by summer the JPL ratios are typically 9000, whereas those over Alaska have fallen to 5500. This reflects the large reduction in meridional transport that occurs between the spring with its strong Westerly flow and the summer with its Easterly flow.

Several of the stratospheric tracers (e.g. HF, HCl) display poleward increases during the summer. To sustain these latitude gradients throughout the summer against mixing processes which would otherwise erode them, one must presume that large-scale descent occurs over the high latitudes during the summer. This view is supported by calculations of the residual mean meridional circulation from heating rates [*Rosenlof,* 1995] which shows that subsidence in the lower stratosphere increases with latitude. The fact that the HF columns outside the vortex show

little seasonal variation is probably largely fortuitous, the reduced meridional transport during the summer being balanced by reduced rates of subsidence.

The $O_3$ column abundance, on the other hand, shows only a slight latitude gradient. How can subsidence enhance the high-latitude column abundances of HF and HCl, but not $O_3$ ? There are two possibilities: (i) chemical destruction of $O_3$, or (ii) transport of $O_3$-poor air from elsewhere. The $O_3$/HF column ratio shows a large increase toward the equator at all stratospheric altitudes, and in the troposphere the HF concentrations should be extremely small due to its high affinity for water. It therefore seems very unlikely that meridional transport could be decreasing the $O_3$/HF ratio at high latitudes. So although transport of $O_3$-poor air from lower latitudes would reduce the $O_3$ column, this air would be even poorer in HF, and so such transport would also reduce the HF column by an even greater fraction. In fact, it is the lack of meridional transport in the summer that allows the different behaviors of $O_3$ and HF to become apparent.

The other possibility is that the source of $O_3$-poor air is the old vortex. However, this seems unlikely for two reasons: Firstly, the vortex only occupies 5% of the area of the Northern hemisphere and so the loss of $O_3$ as the vortex remnants are mixed into mid-latitude airmasses can only be a few per-cent. Secondly, the amount of Arctic ozone depletion is highly variable from winter to winter, and yet the summertime $O_3$ loss is of a similar magnitude every year.

The final transport-related possibility is that the summertime $O_3$ loss is due to vertical transport. While it is certainly true that large scale ascent would reduce column $O_3$, it would reduce column HF by a similar or even greater fraction. The constancy of the HF column with time, together with the constancy of the $O_3$/HF ratio with altitude, therefore rule out large scale ascent (or descent) as being the cause of the $O_3$ loss.

We therefore address the possibility that the summertime $O_3$ loss was the result of chemistry. The decrease in the $O_3$/HF ratio between the May and the July balloon flights for altitudes below 24 km is certainly suggestive of a chemical loss. And although these balloon flights provide only two data points, the ground-based column data corroborate the balloon results and demonstrate that the $O_3$/HF column ratio declined steadily throughout the late spring and summer. The chemical loss explanation is also supported by model calculations [*Salawitch et al.*, 1999], constrained by the MkIV balloon profiles, which show $O_3$ loss rates of up to 10% per month in early summer at altitudes below 25 km. Since at higher altitudes the $O_3$ loss rates are substantially smaller, this balloon-derived value is perfectly consistent with the summertime observations of the $O_3$/HF column ratio from both Fairbanks and Ny Alesund which exhibit a 5% per month decrease between days 150 and 250. Note that this value is probably an underestimate of the actual chemical loss because even the weak summertime meridional transport would have undoubtedly mixed some mid-latitude air, rich in $O_3$ compared to HF, into the high latitudes.

## Summary and Conclusions.

Ground-based solar absorption spectra from two high latitudes sites, Fairbanks and Ny Alesund, have been analyzed to determine the vertical column abundances of various trace gases during the spring and summer of 1997. Additionally, balloon and satellite profiles of $O_3$ and HF have been analyzed to show that at high latitudes the $O_3$ and HF profiles are very similar in shape, at least in the 10-30 km altitude range where most of the vertical column abundance resides. Therefore, ratioing measured column abundances against those of HF, removes column variations arising from transport (e.g. movement of the vortex), making it possible to also

determine the real temporal changes in the column abundances of the measured gases. We infer large depletions of $O_3$, HCl, and $ClNO_3$ inside the vortex during March and April. Even outside the vortex, significantly perturbed chemical partitioning existed in late March with enhanced $ClNO_3$ and depleted HCl abundances. However, during April, the $ClNO_3$ column abundances declined to normal values, while the HCl increased by an approximately equal amount.

During spring and summer 1997 the $O_3$ column abundance above Fairbanks declined by over 35%, with most of this loss occurring in early summer. Since this change was accompanied by no significant change in the HF burdens, we must conclude that it was entirely chemical in origin. This interpretation is supported by balloon and satellite profiles of $O_3$ and HF which show that the $O_3$/HF ratio decreased poleward throughout the stratosphere. The observed 35% decrease in column $O_3$ is therefore probably an underestimate of the true chemical loss of $O_3$ during spring and summer 1997, since any meridional transport would have helped to mitigate the decrease in the $O_3$/HF column ratio. Our estimate of the column ozone loss rate of 5% per month during May and June is consistent with photochemical calculations constrained by balloon measurements of NO and $NO_2$ [*Salawitch et al.*, 1999]. This indicates that high latitude summertime ozone loss is a natural phenomenon due to the amount of stratospheric $NO_X$ being enhanced during the long polar days. Indeed, the $NO_X/NO_Y$ column ratio peaked at a value of 0.4 in July 1997. It is notable that although the summertime $O_3$ loss rates are much slower than those in the late winter, they have several months to operate and so their cumulative effect (35% $O_3$ loss) over the summer is comparable with, or greater than, the $O_3$ loss during an average winter.

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## Figure Captions.

1) Vertical column abundances measured above Fairbanks, Alaska, in 1997. The upper panel (a) shows measurements of column $O_3$ made by the JPL MkIV interferometer (orange diamonds), the Brewer Spectrophotometer (green triangles) and the Earth-Probe TOMS instrument (blue dots with connecting line). The lower panel (b) shows measurements of column HF measured by MkIV.

2) HF-$N_2O$ vmr correlations from mid-latitude (empty symbols) and high latitude (filled symbols) MkIV balloon flights. FTS = Ft. Sumner, New Mexico ($34^oN$); DAG = Daggett, California ($34^oN$); LYL = Lynn Lake, Manitoba ($57^oN$); FAI = Fairbanks, Alaska ($65^oN$). The top panel (a) shows the raw HF measurements, whereas the lower panel (b) shows the same data but after the HF has been detrended by assuming a 5% annual increase.

3) VMR profiles of $O_3$ and HF measured during MkIV balloon flights above Fairbanks, Alaska, on 8 May 1997 (upper panels) and 8 July 1997 (lower panels). The HF profiles has been scaled by a factor 5000 to make them more easily compared with the $O_3$ profiles. A single sunrise profile (stars) was obtained from the May flight, whereas both ascent (up triangles) and descent (down triangles) profiles were obtained from the July flight.

4) Concentration profiles of $O_3$ and HF measured during MkIV balloon flights above Fairbanks, Alaska, on 8 May 1997 (upper panels) and 8 July 1997 (lower panels). The symbols and colors are as for figure 3.

5) MkIV balloon vmrs of $O_3$ and HF from various mid- and high-latitude flights. The upper panel

(a) shows the direct $O_3$-HF correlation, whereas the lower panel (b) shows the $O_3$/HF ratio as a function of potential temperature.

6) Version 18 HALOE profiles of $O_3$ and HF measured during late April and early May 1997. These data cover latitudes from $59^{o}$S to $69^{o}$N with a gap from $45^{o}$-$56^{o}$N, and have been color-coded according to the latitude range in which they were observed, in the same manner as Figure 5. The thick colored lines represent the average profile for that latitude bin. These data confirm that the $O_3$/HF ratio decreases poleward throughout the stratosphere.

7) Time series of calculated (a) PV, and observations of column (b) HF, (c) $O_3$, (d) $O_3$/HF, (e) HCl, (f) HCl/HF, (g) $ClNO_3$, (h) $ClNIO_3$/HF, (i) $NO_2$, (j) $NO_2$/HF, (k) $HNO_3$, (l) $HNO_3$/HF, (m) $NO_X$ , and (n) $NO_X/NO_Y$ above Fairbanks, Lynn Lake, and Ny Alesund. For each gas, the ratio of its column abundance to that of HF is also shown in the right hand panels.

Figure 1: Column $O_3$ above Fairbanks during POLARIS

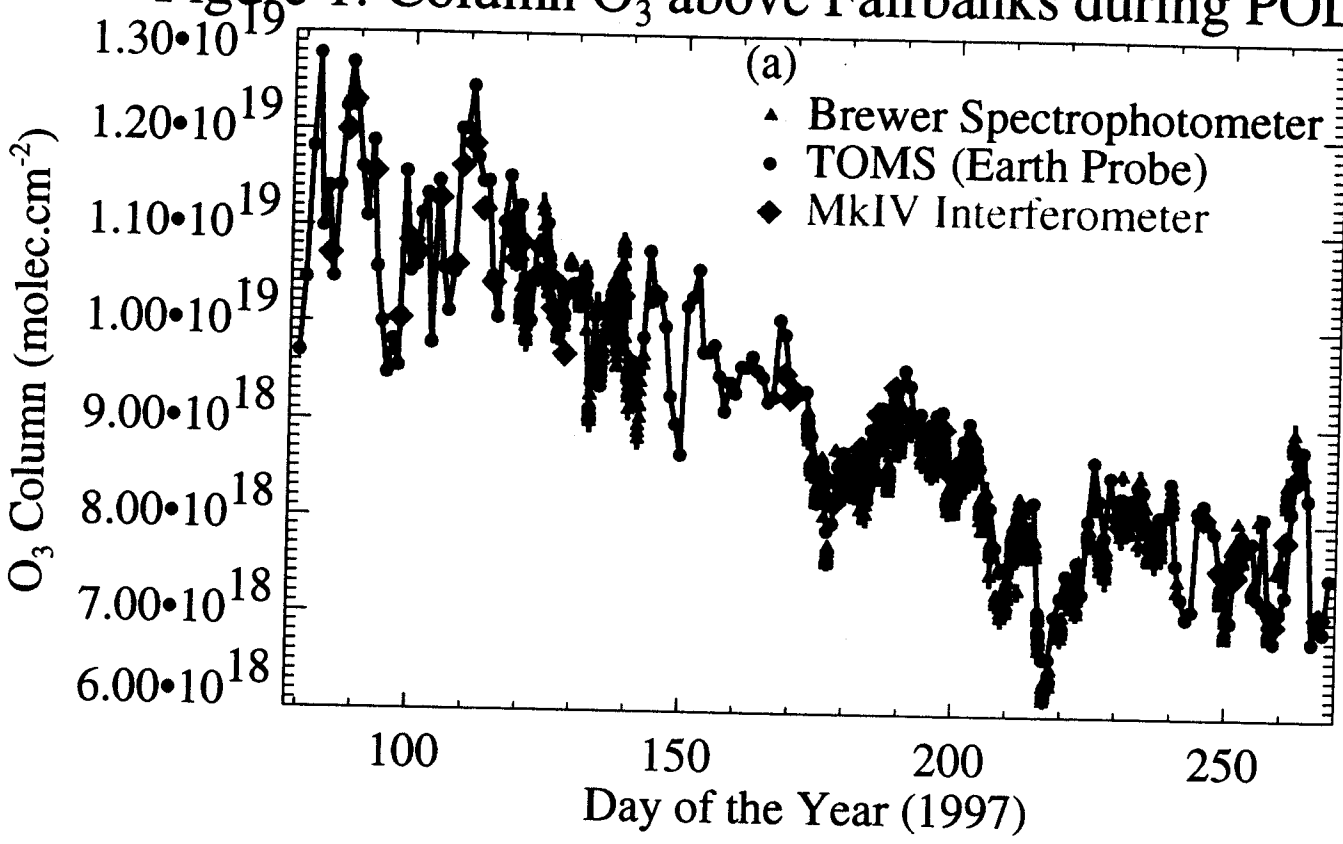


Figure 1: Column HF above Fairbanks during POLARIS

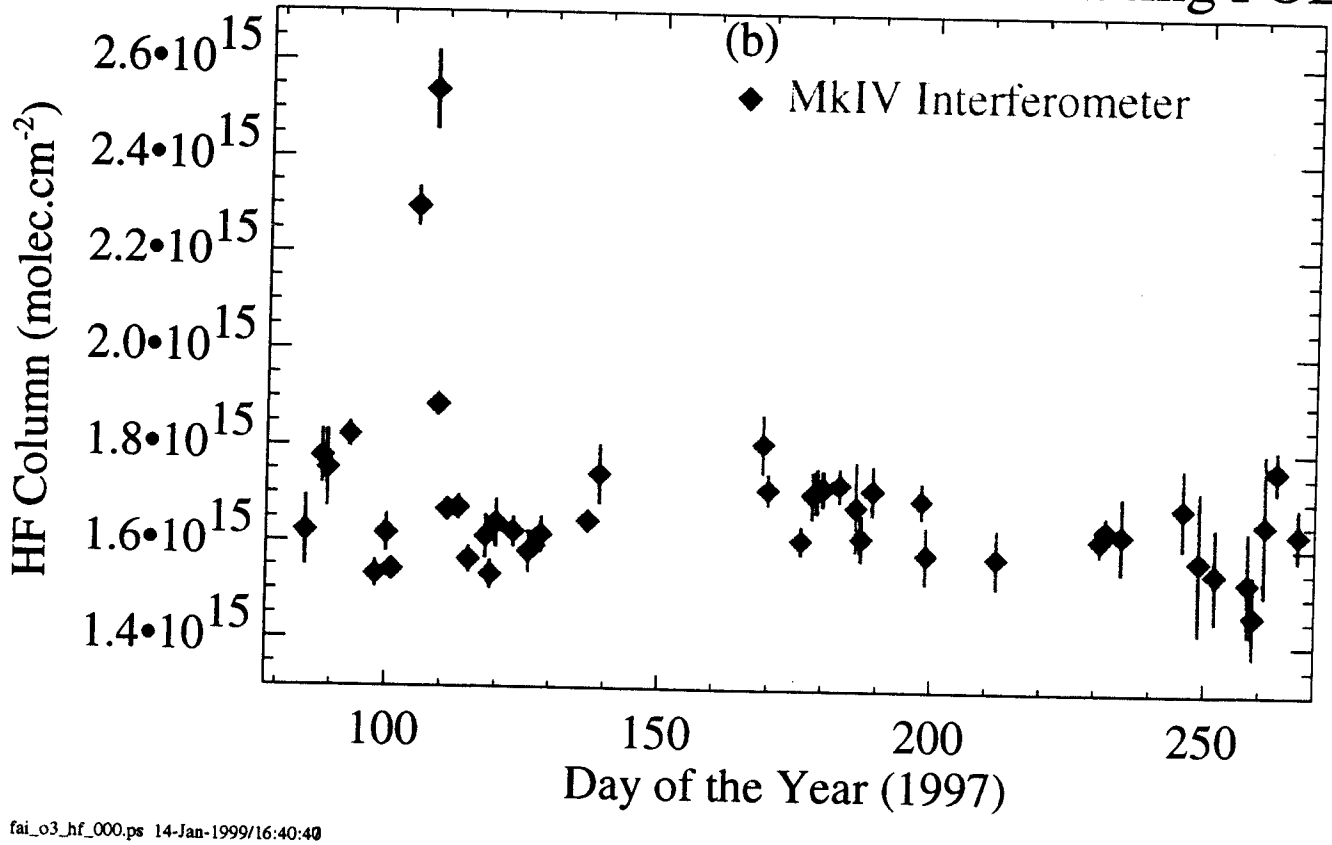


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Figure 2a. MkIV balloon observations.

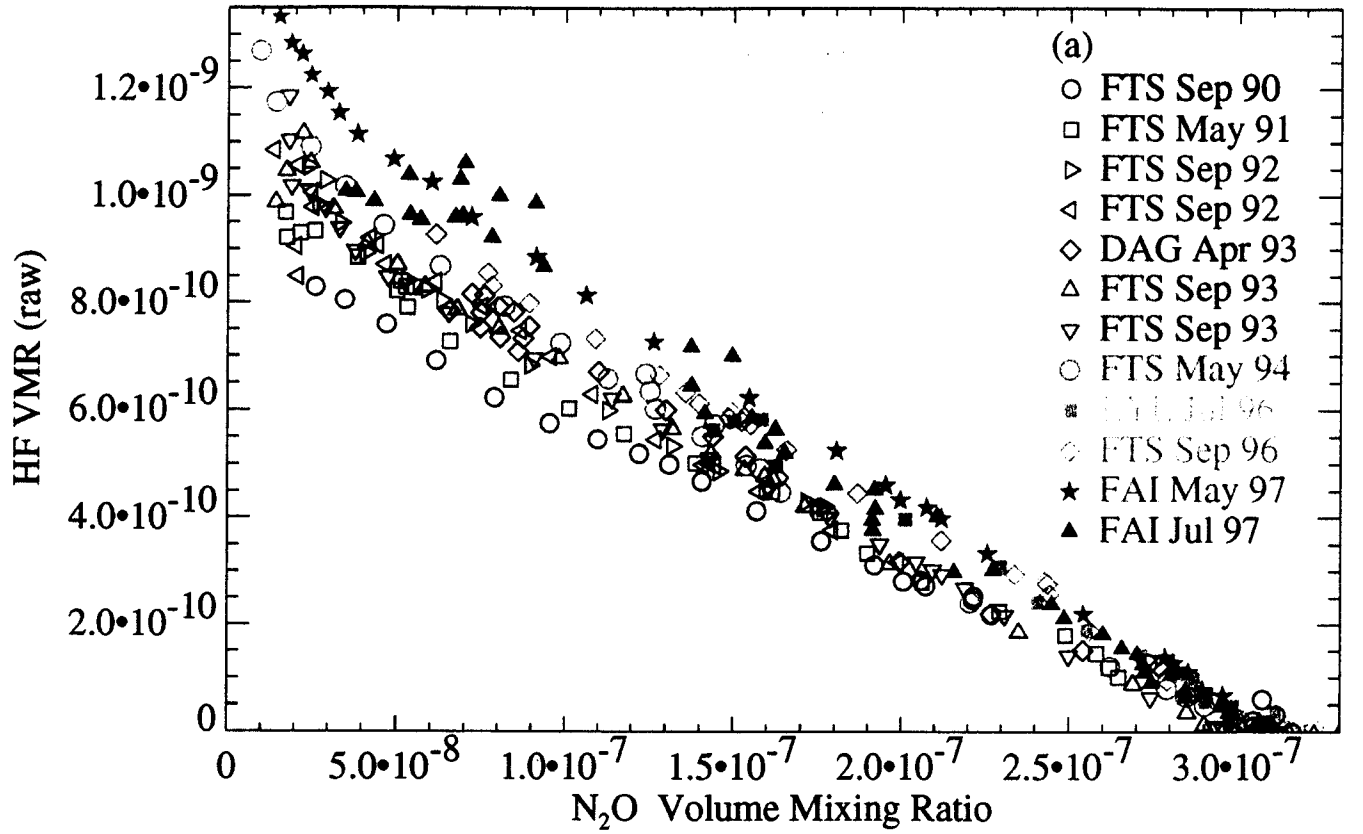


Figure 2b. MkIV balloon observations

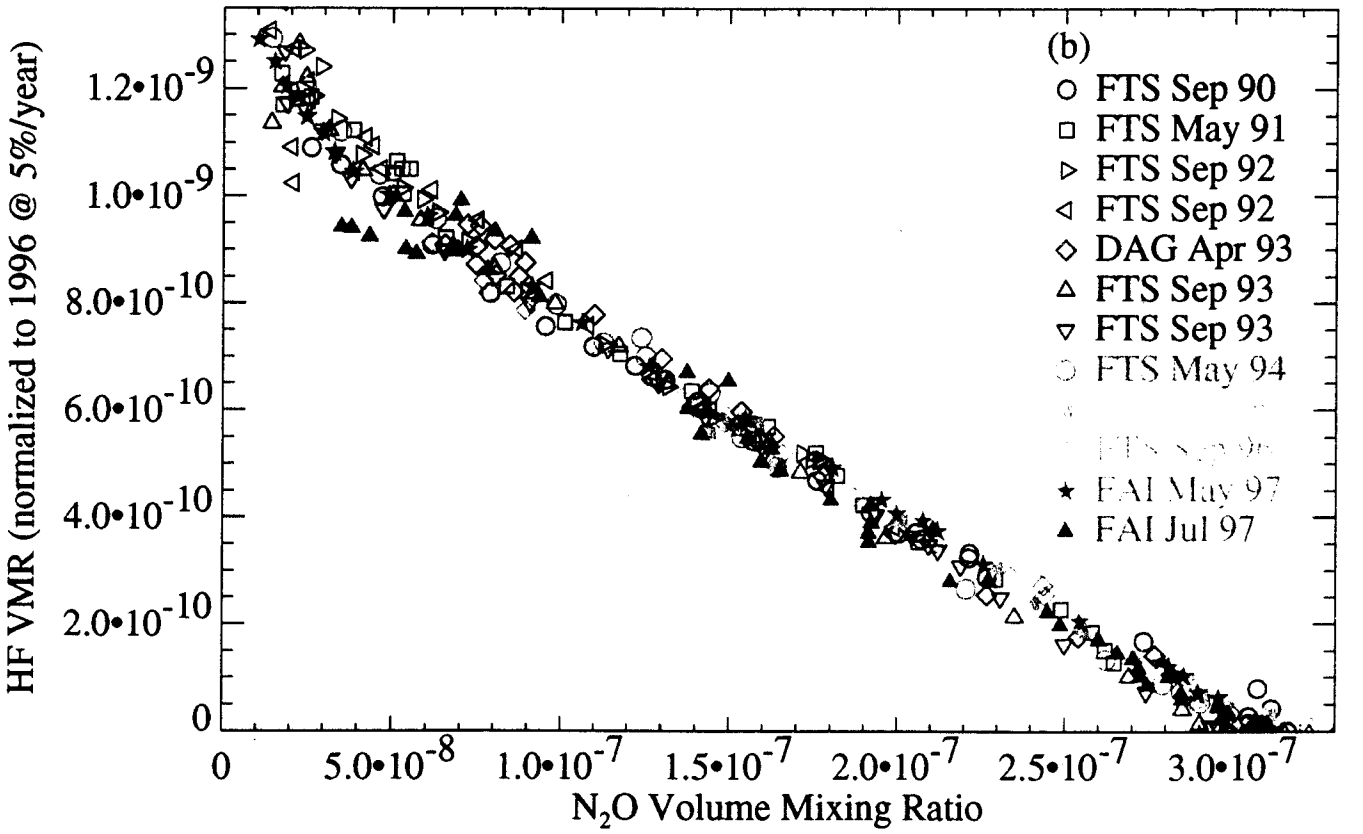


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Fig 3a: MkIV balloon profiles of $O_3$ and HF above Fairbanks, 8-May-199

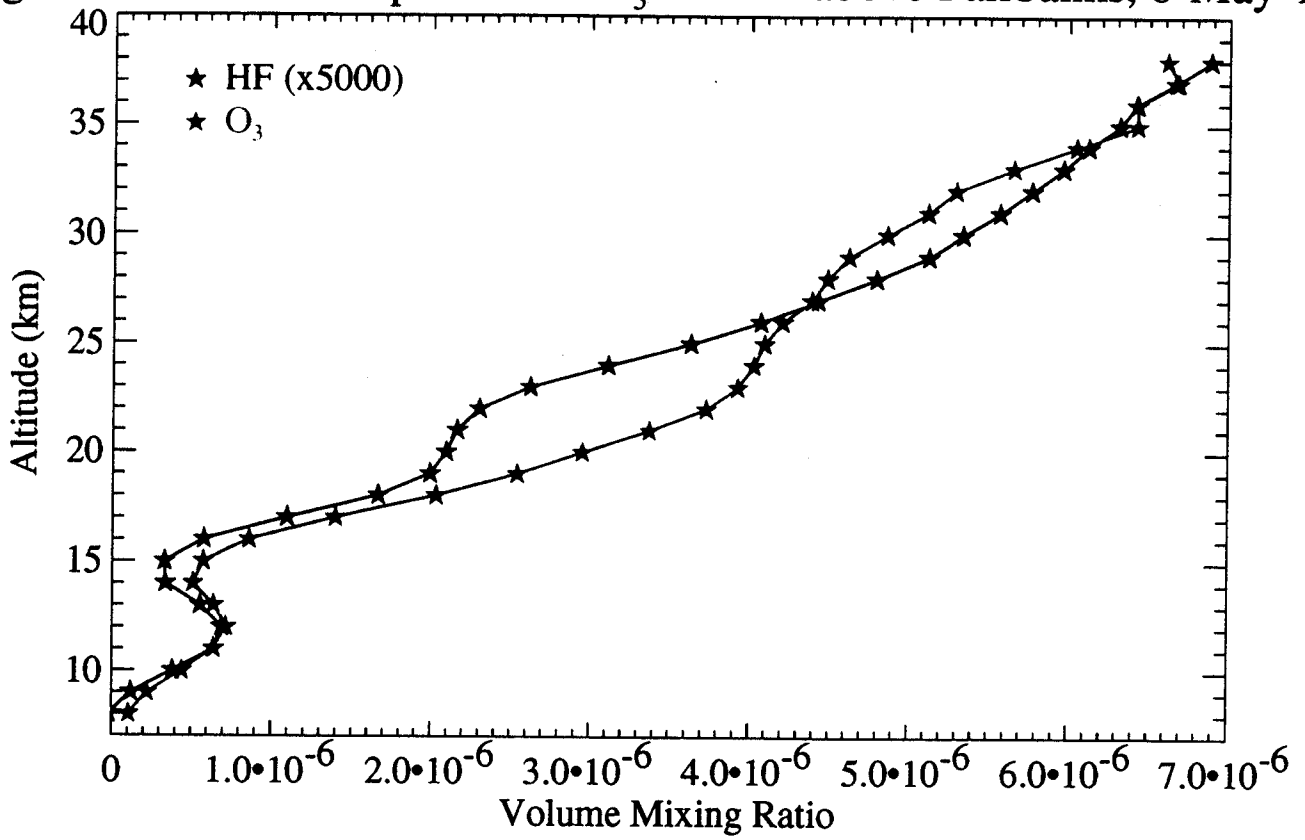


Fig 3b: MkIV balloon profiles of $O_3$ and HF above Fairbanks, 8-Jul-1997

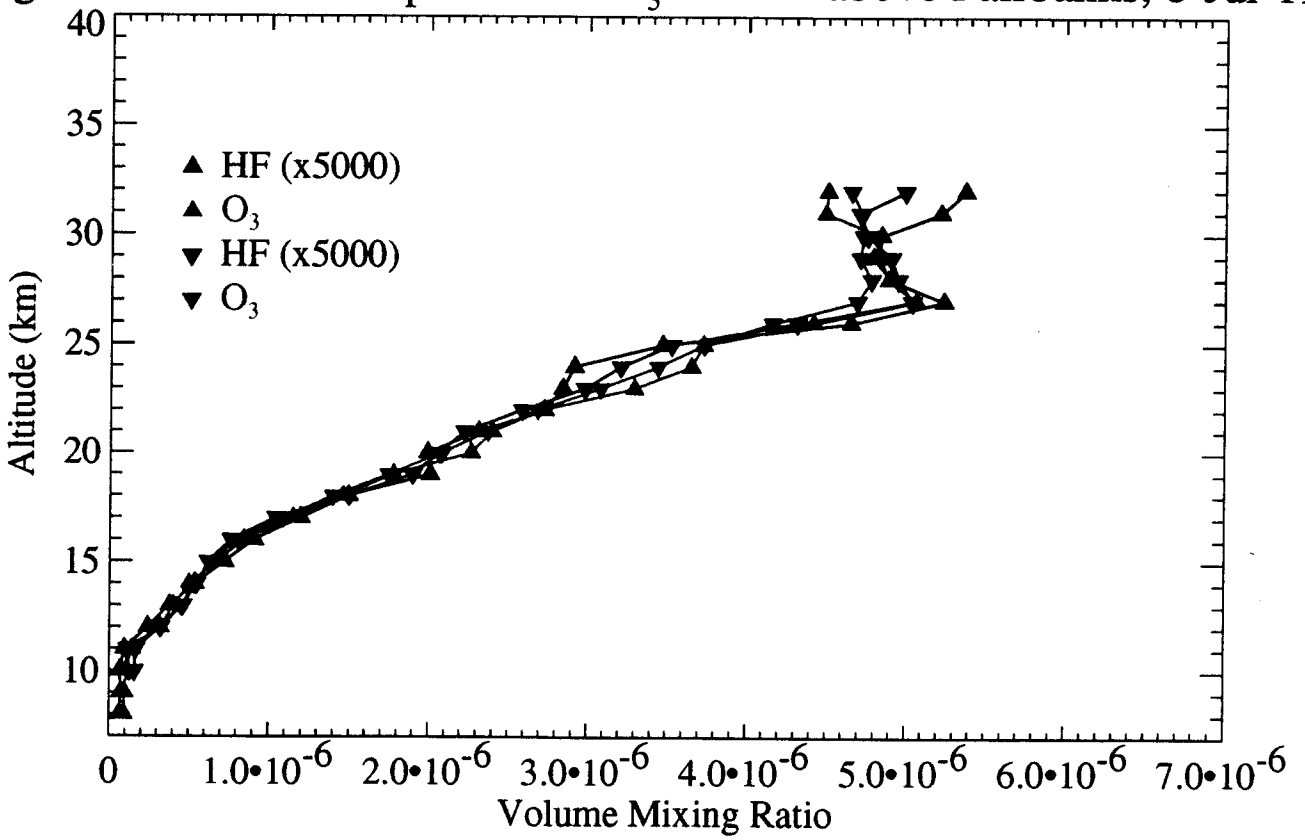


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Fig 4a: MkIV balloon profiles of $O_3$ and HF above Fairbanks, 8-May-199

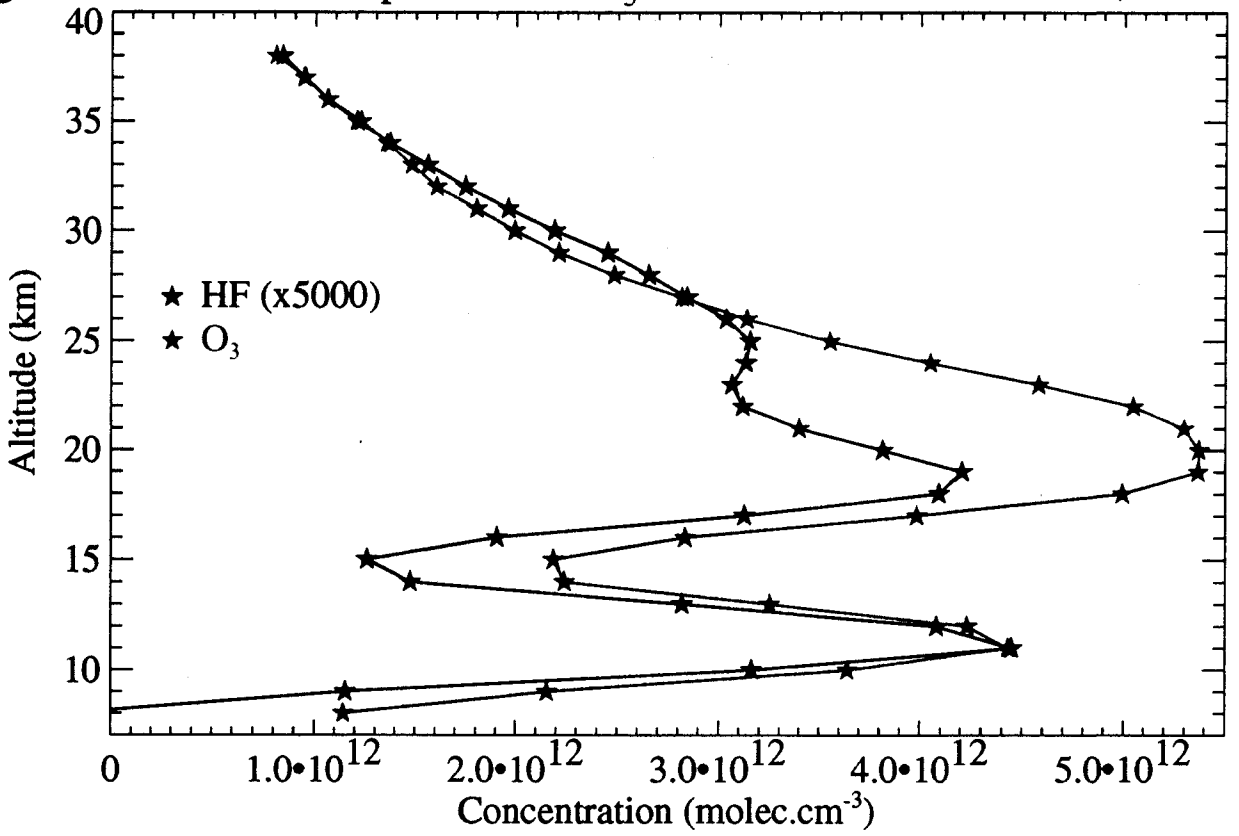


Fig 4b: MkIV balloon profiles of $O_3$ and HF above Fairbanks, 8-Jul-1997.

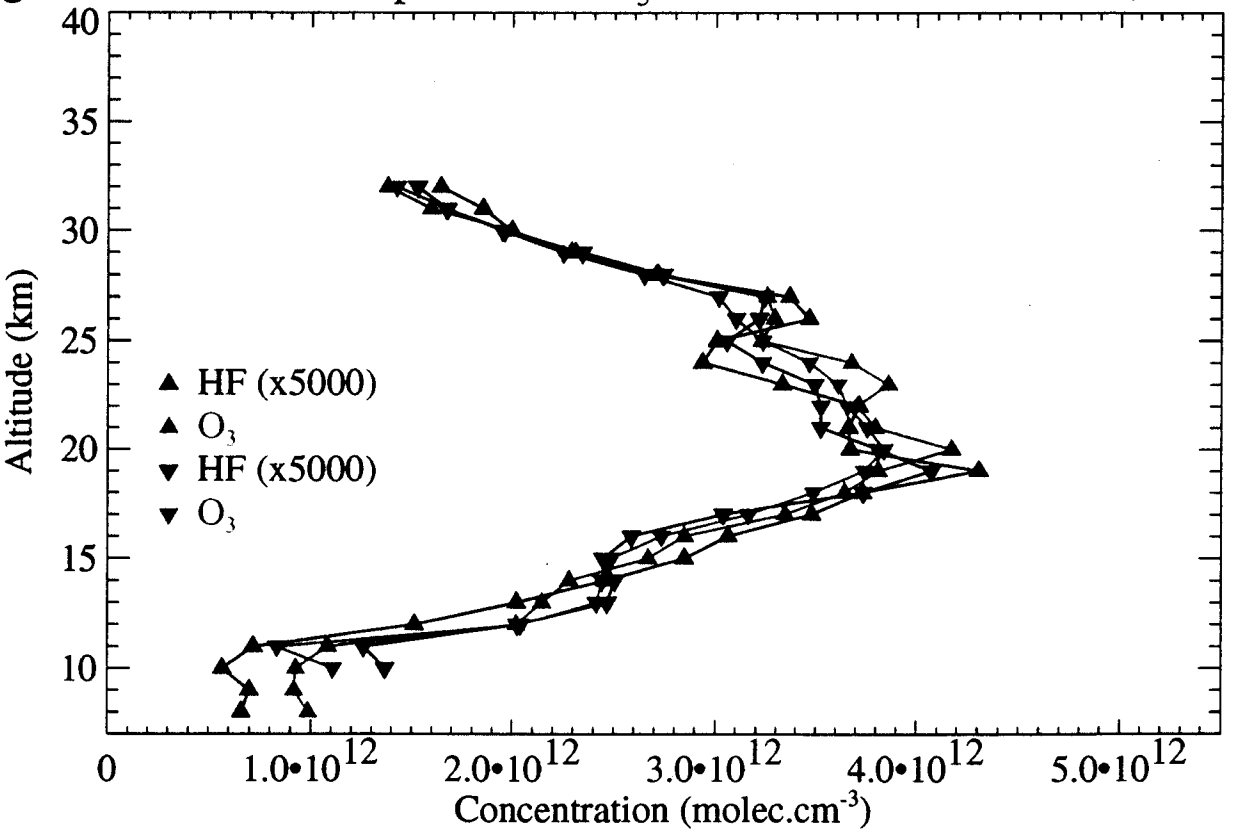


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Figure 5a. MkIV balloon observations.

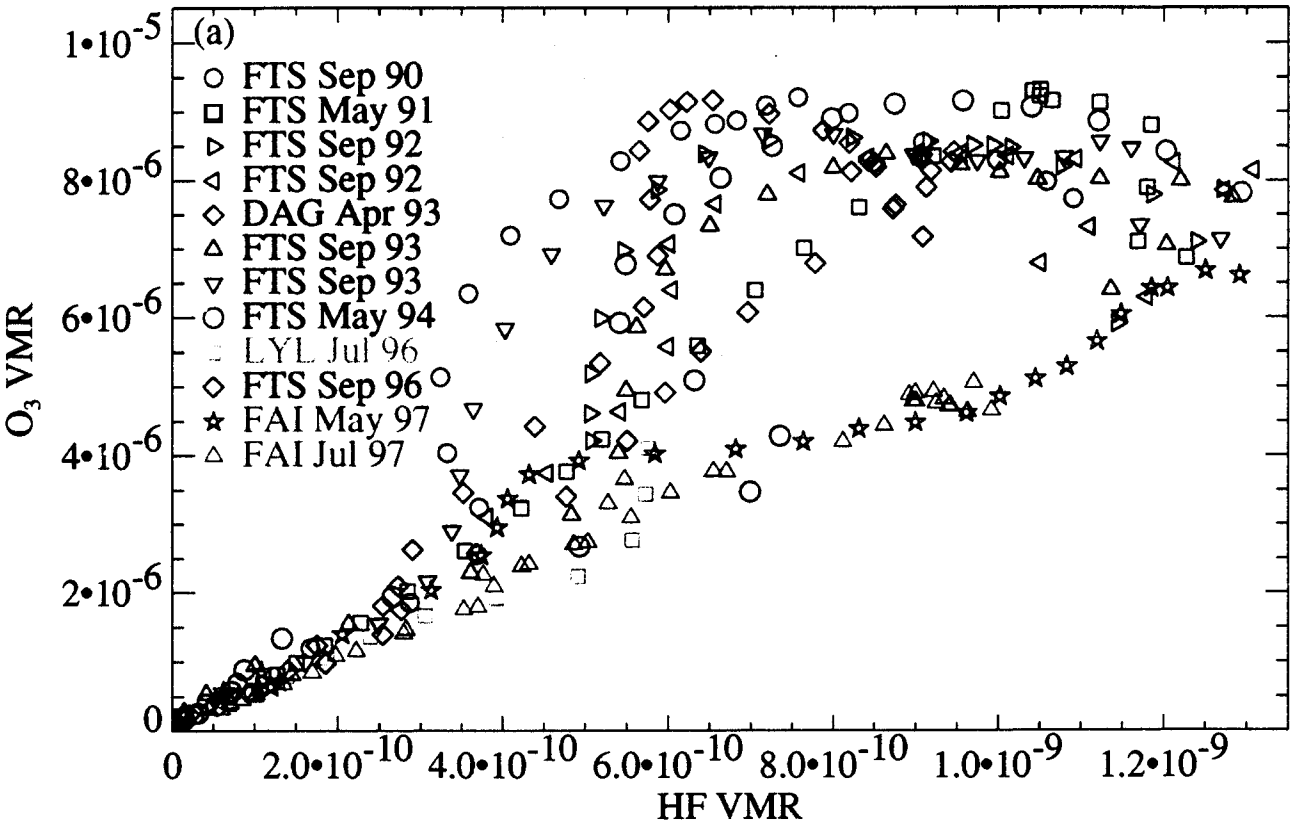


Figure 5b. MkIV balloon observations.

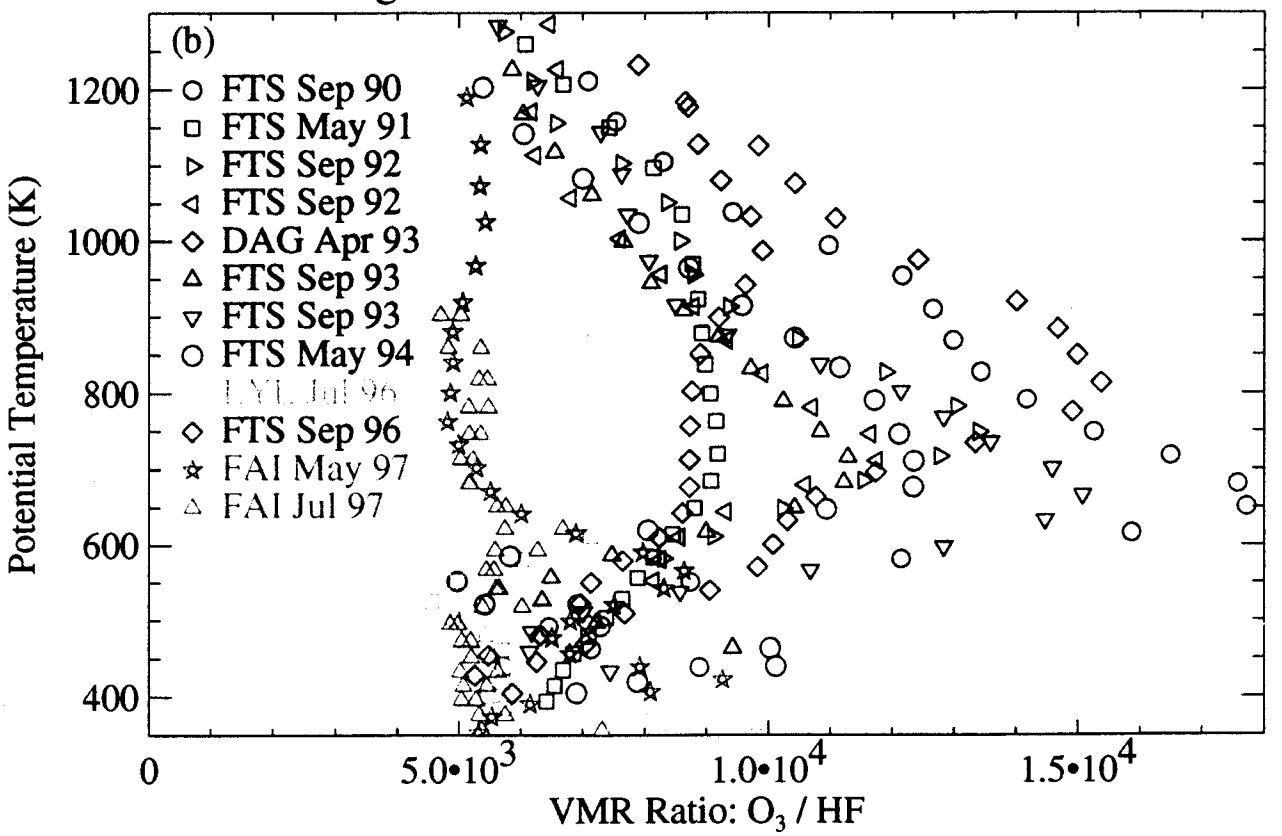


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Figure 6(a): HALOE Northern Hemisphere Observations in 1997

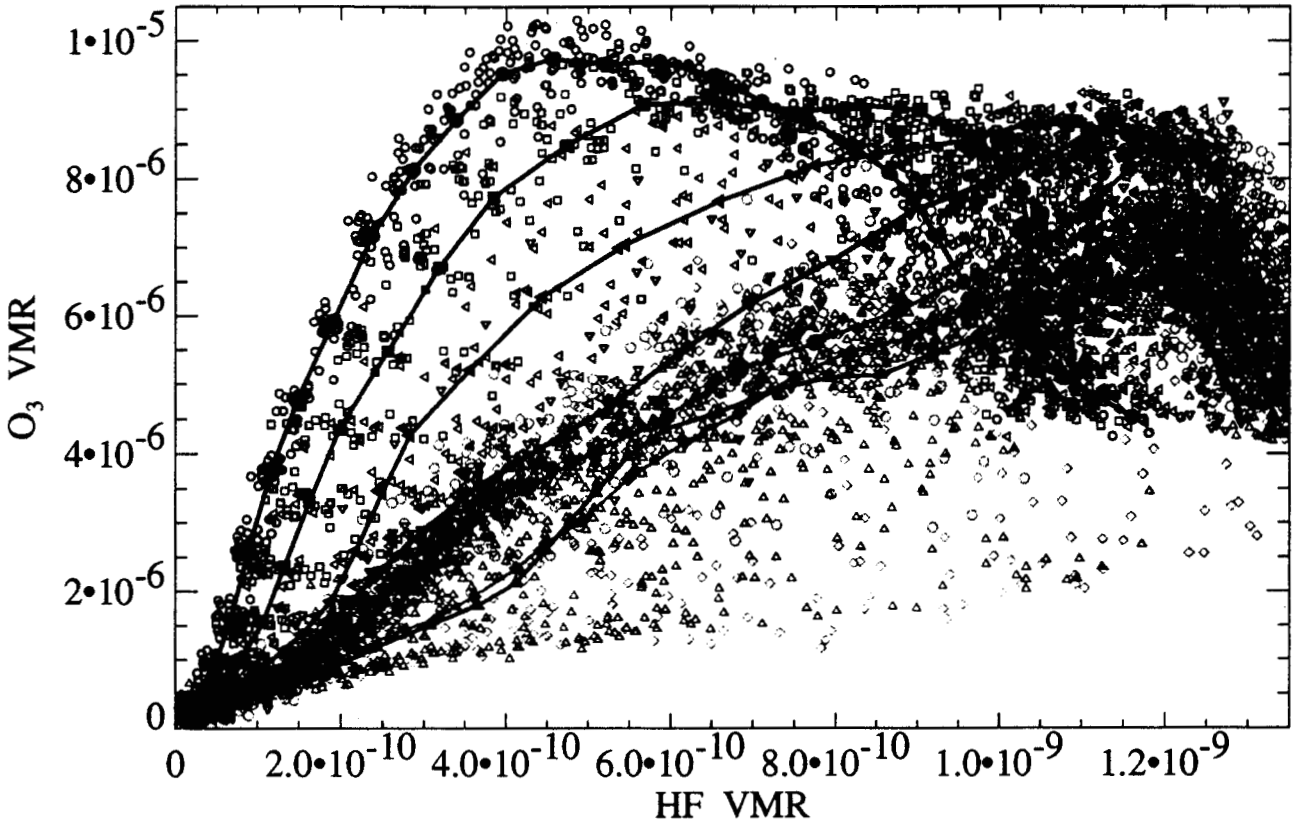


Figure 6(b): HALOE Northern Hemisphere Observations in 1997

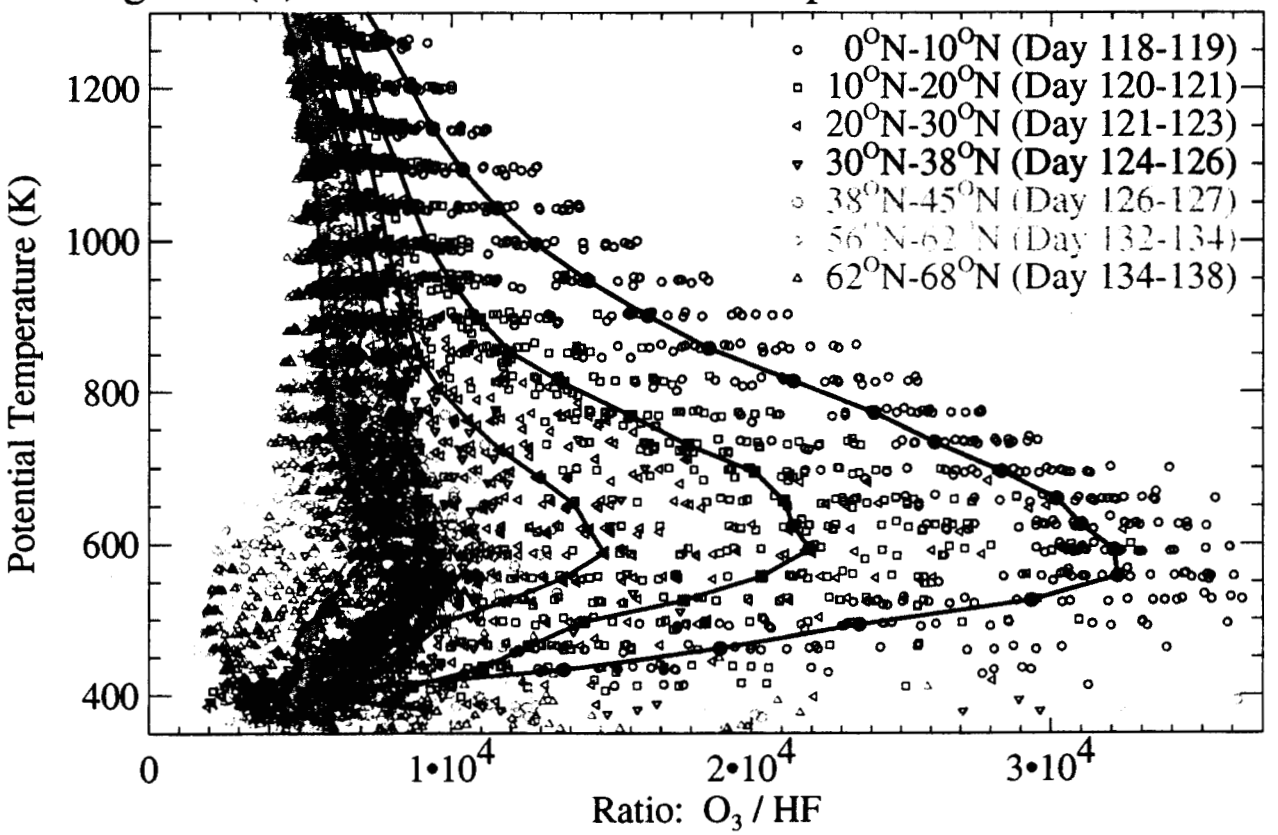


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Figure 6(c): HALOE Southern Hemisphere Observations in 1997

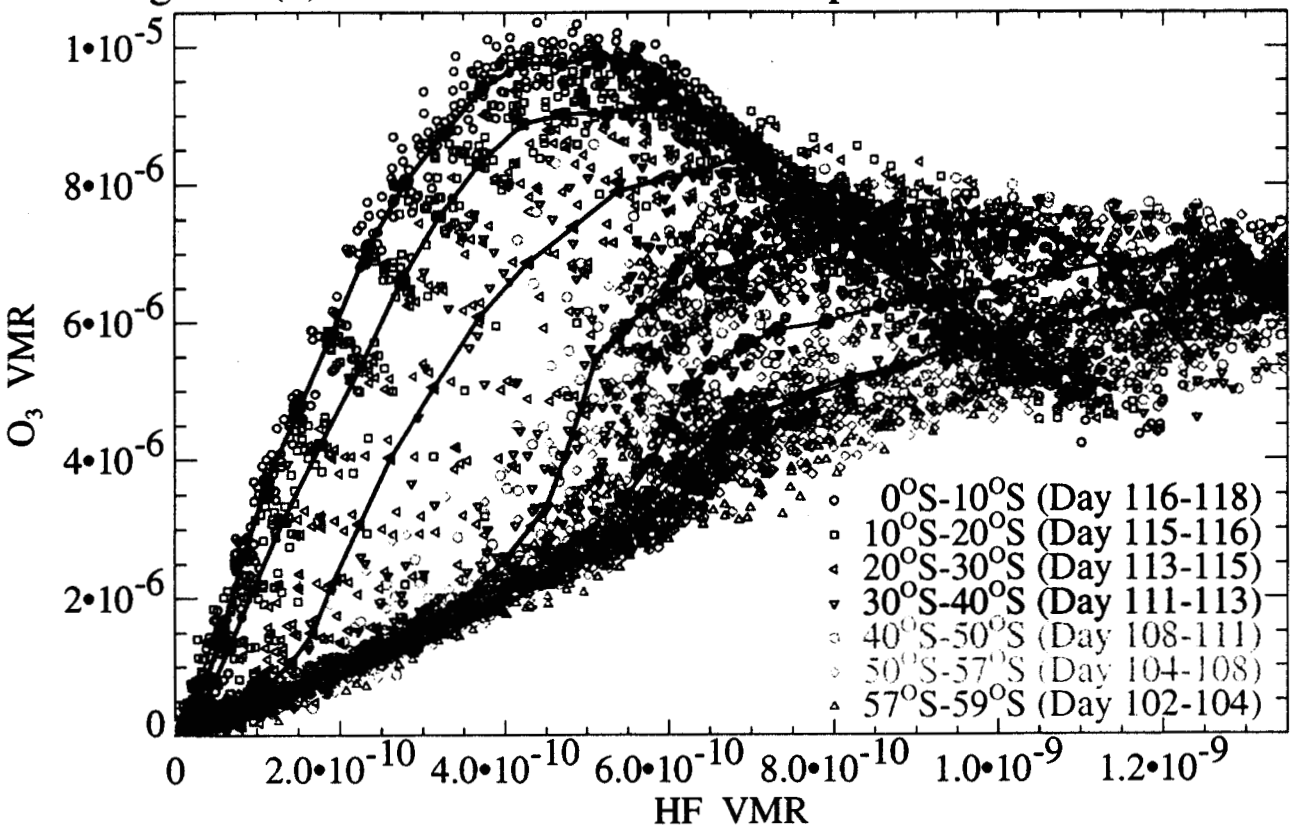


Figure 6(d): HALOE Southern Hemisphere Observations in 1997

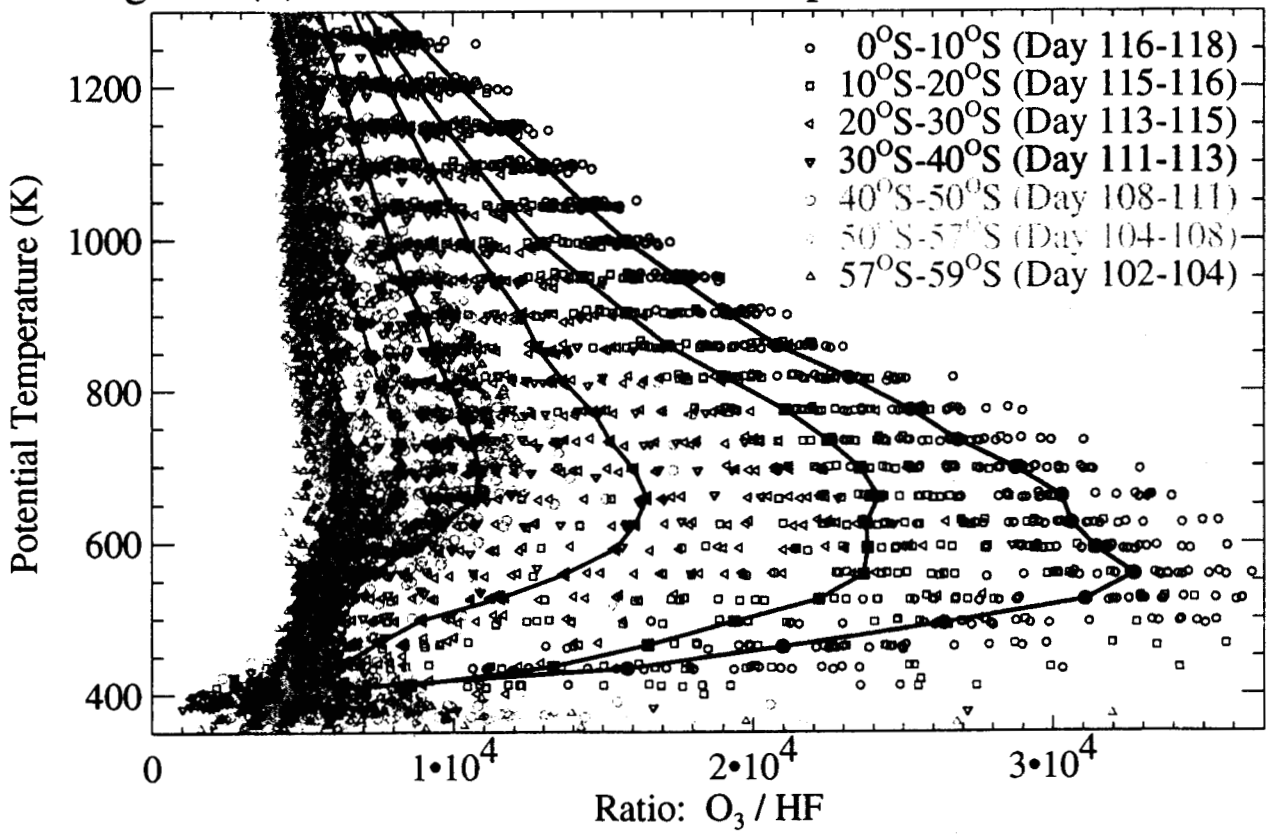


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Figure 7 remove *

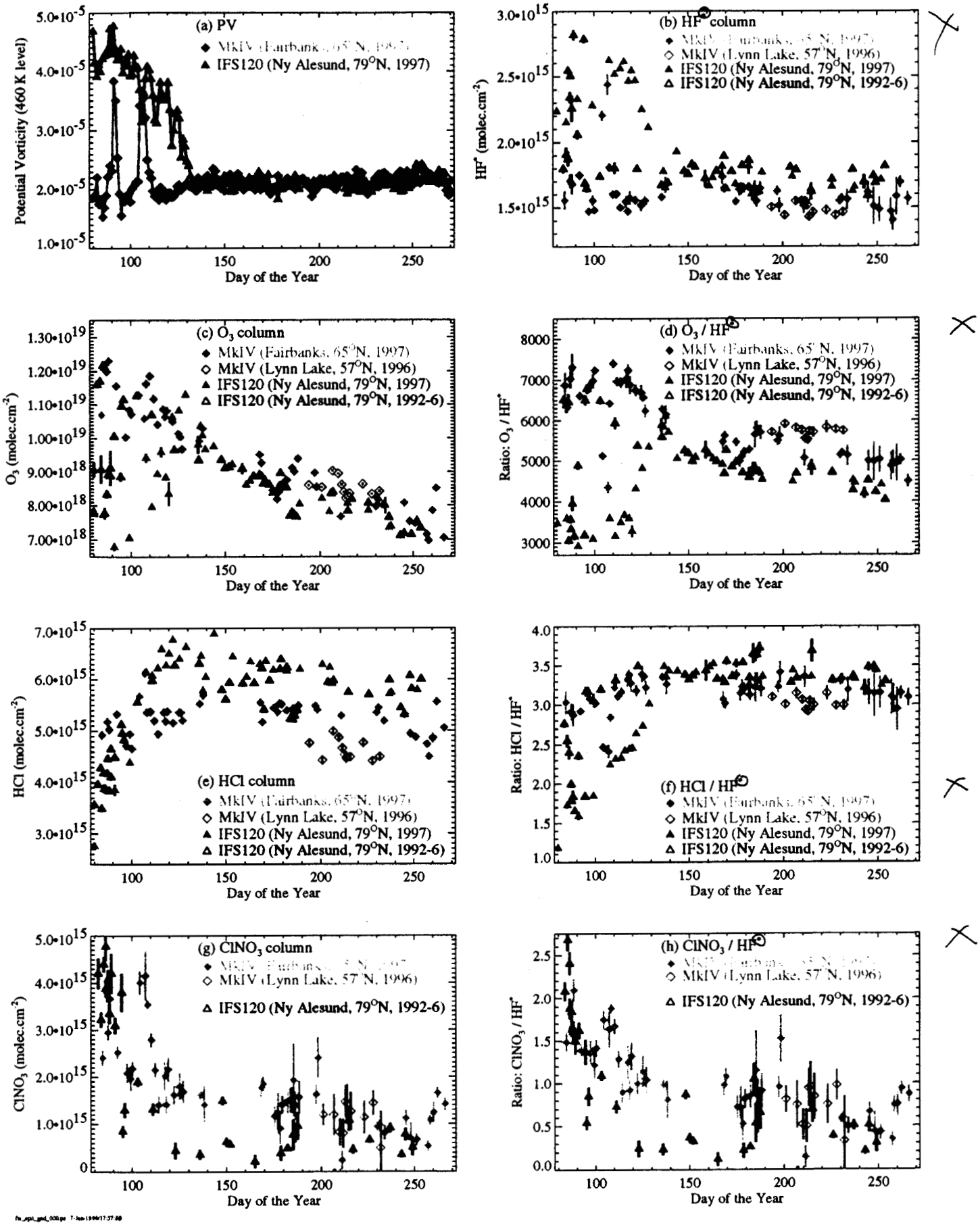
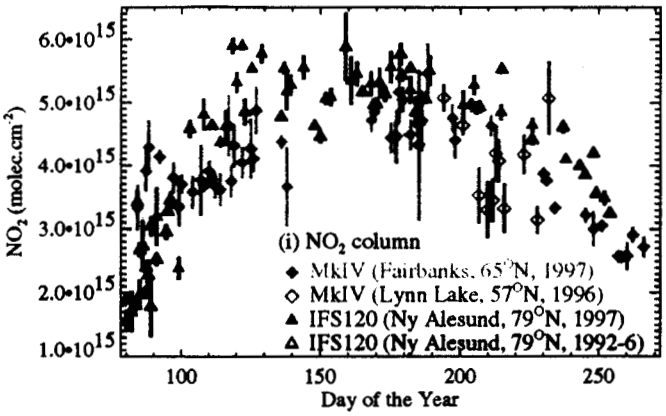
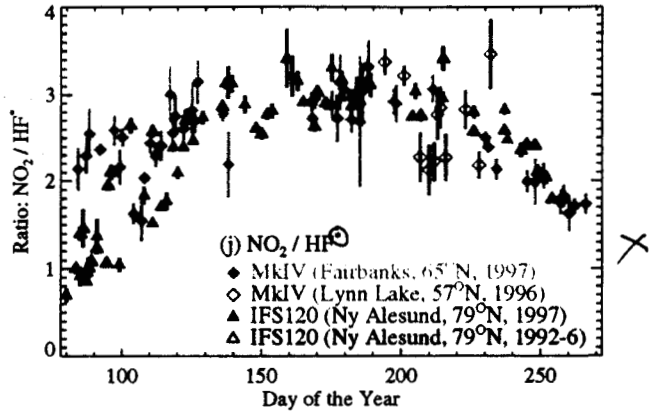
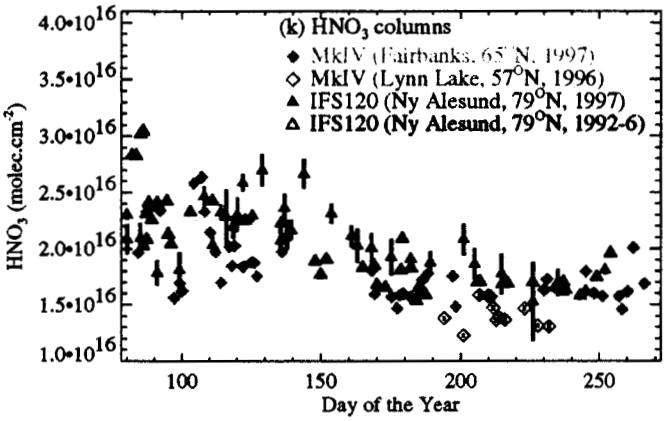
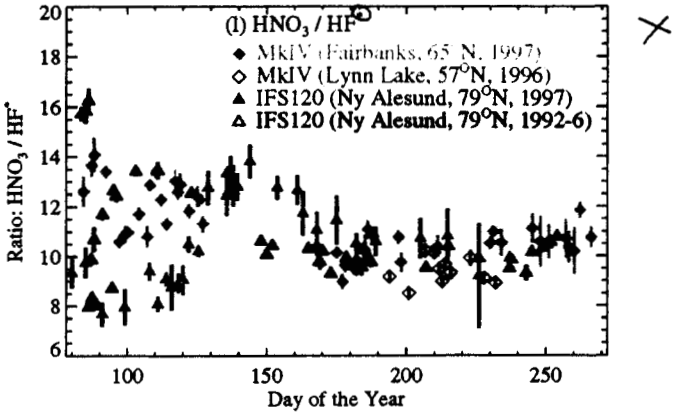


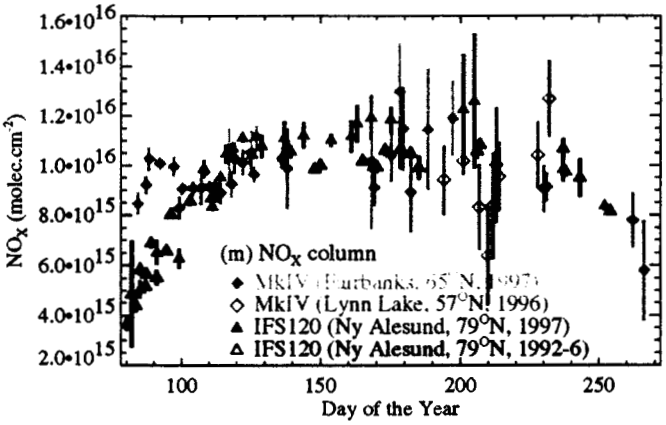
Figure 7

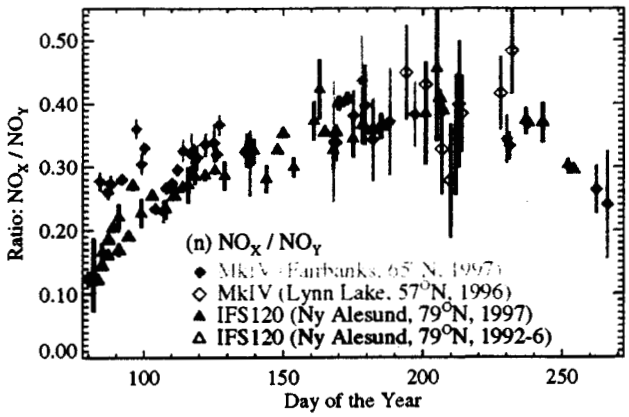

(i) $NO_2$ column
MkIV (Fairbanks, 65°N, 1997)
MkIV (Lynn Lake, 57°N, 1996)
IFS120 (Ny Alesund, 79°N, 1997)
IFS120 (Ny Alesund, 79°N, 1992-6)
$NO_2$ (molec.cm$^{-2}$)
Day of the Year


(j) $NO_2$ / HF
MkIV (Fairbanks, 65°N, 1997)
MkIV (Lynn Lake, 57°N, 1996)
IFS120 (Ny Alesund, 79°N, 1997)
IFS120 (Ny Alesund, 79°N, 1992-6)
Ratio: $NO_2$ / HF
Day of the Year


(k) $HNO_3$ columns
MkIV (Fairbanks, 65°N, 1997)
MkIV (Lynn Lake, 57°N, 1996)
IFS120 (Ny Alesund, 79°N, 1997)
IFS120 (Ny Alesund, 79°N, 1992-6)
$HNO_3$ (molec.cm$^{-2}$)
Day of the Year


(l) $HNO_3$ / HF
MkIV (Fairbanks, 65°N, 1997)
MkIV (Lynn Lake, 57°N, 1996)
IFS120 (Ny Alesund, 79°N, 1997)
IFS120 (Ny Alesund, 79°N, 1992-6)
Ratio: $HNO_3$ / HF
Day of the Year


(m) $NO_X$ column
MkIV (Fairbanks, 65°N, 1997)
MkIV (Lynn Lake, 57°N, 1996)
IFS120 (Ny Alesund, 79°N, 1997)
IFS120 (Ny Alesund, 79°N, 1992-6)
$NO_X$ (molec.cm$^{-2}$)
Day of the Year


(n) $NO_X$ / $NO_Y$
MkIV (Fairbanks, 65°N, 1997)
MkIV (Lynn Lake, 57°N, 1996)
IFS120 (Ny Alesund, 79°N, 1997)
IFS120 (Ny Alesund, 79°N, 1992-6)
Ratio: $NO_X$ / $NO_Y$
Day of the Year